Effects of some surfactants on foliar impaction and retention of monosize water droplets

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Abstract: The impaction and retention behavior of low-velocity (below $3\,m\,s^{-1}$) monosize droplets (100–1000 µm diameter) containing either water or aqueous surfactant solutions was examined on wettable and water-repellant leaf surfaces using a high magnification video system. Mapping of bounce trajectories provided a history of droplet behaviour from first impact to final retention on, or escape from, a leaf, and yielded velocity thresholds for capture or bounce following impact of any droplet. Water droplets were captured on water-repellant leaves only when their pre-impact velocity fell below $0.25\,m\,s^{-1}$, so that even small (120 µm) low-velocity ($0.57\,m\,s^{-1}$) droplets bounced between two and six times before finally being retained. Surfactant addition invariably reduced the number of bounces between first impact and retention, and increased the velocity threshold for capture following impact. The physical parameters of droplets, as expressed by Reynolds (Re) and Weber (We) numbers, are discussed and the trajectory data shown to generate two relationships between Re and We which define the transition from capture to bounce following impact.

Keywords: adjuvants; impact; retention; monosize droplets

A wide variety of adjuvants are used to increase the efficiency of spray delivery of foliage-applied agrochemicals from hydraulic nozzles. Although these products are known to alter the physical characteristics of spray droplets in different ways, detailed information about their effects on impaction is lacking. Some general predictions about their performance using, for example, dynamic surface tension and volume median diameter can be obtained from whole-plant spray retention data.[1,2] However, the total effect of adjuvants on spray delivery to a target is the sum of a number of interacting factors, namely liquid atomisation, droplet transport and drift, droplet impact on the target and retention of droplets after deposition.

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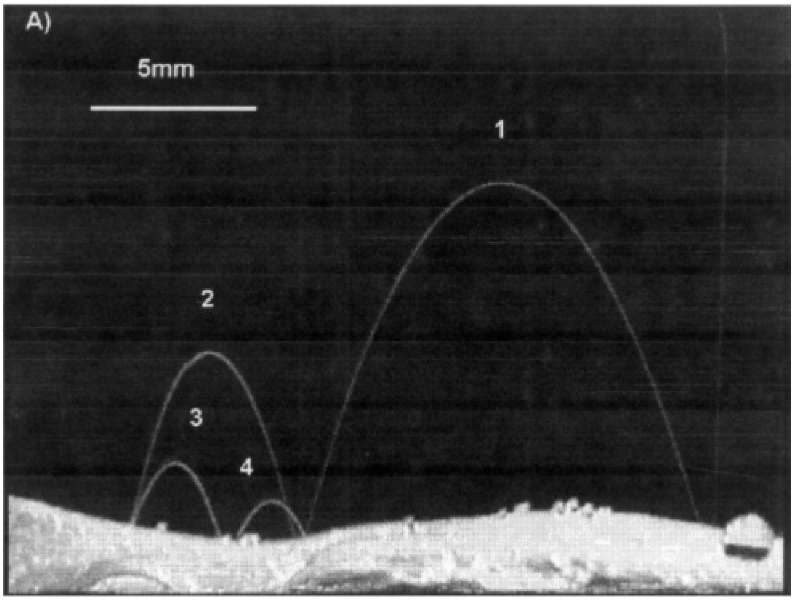
In the present work, we have studied the impaction behaviour of monosize water droplets on the adaxial surface of leaves of pea (*Pisum sativum* cv Meteor), a crop with waxy water-repellent leaves, and field bean (*Vicia faba* L cv Maris Bead), a crop with highly wettable leaves. Plants were raised from seed in pots of compost in a glasshouse and used 20 to 30 days after sowing; single fully expanded leaves were excised immediately before use. Two surfactant types whose physical and spray retention properties are known were used;[1–3] a series of C_{13}/C_{14} polyoxyethylene primary alcohol (AE) surfactants (Marlipal 34 series ex Hüls, Germany) with ethylene oxide (EO) contents of 6, 11 and 20 and an 8EO organosilicone (OS) surfactant (Silwet L-77, ex OSi Specialities Inc, USA). Surfactants were tested in water at 0.2 and 1 $g\,litre^{-1}$, and compared with water alone. A water-soluble fluorescent tracer, Tinopal CBS-X (ex Ciba-Geigy, UK), was also added to all solutions at 0.2 $g\,litre^{-1}$ for deposition and spreading studies that will be reported elsewhere.

Monosize droplets were generated using a device similar to that described by Reichard.[4] A piezoelectric crystal mounted on a brass plate forms a deformable wall in a liquid chamber so that voltage pulses of different magnitude and duration supplied to the crystal cause the ejection of variable sized droplets from the nozzle (orifice diameter 50, 100 or 200 µm) at rates varying from a single event to two per second, travelling 40 mm from nozzle to target. Droplet sizes were recorded using water-sensitive paper (ex Ciba-Geigy, UK) and their size and velocity before impact measured using a high-magnification video system (JVC and Synoptics, UK) and verified using a phase-Doppler particle analyser (Aerometrics Inc, USA). Droplets with diameters of 100 to 1000 µm could be produced with velocities before first impact of $<3\,m\,s^{-1}$. Voltage pulses were adjusted to avoid secondary droplet generation, giving a set of discrete size and velocity combinations.

The video system was used in 'open shutter' mode to capture the trajectories of droplets impacting on adaxial leaf surfaces, with the leaf surface at right angles to the direction of droplet travel. Most impacts were targeted onto a dry surface but some impacts onto surfaces previously wetted by droplets were recorded. At the low speeds used, there was no droplet shatter on impact. Where bounce occurred, droplet trajectories followed a series of one or more bounces with a classical parabolic path (Fig 1A). For each bounce, the maximum height attained defined the vertically downward velocity of the next impact. Furthermore, for each droplet-size/spray solution combination, a bounce height condition was found such that below one height all droplets were captured at next impact, above another height all droplets bounced, while between these two heights either capture or bounce could occur. Thus, bounce heights yielded two pre-impact velocity criteria, a capture



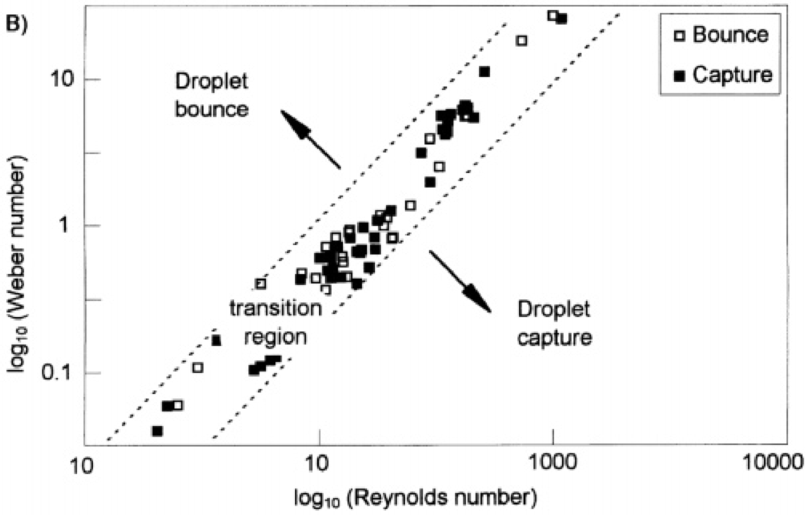


Figure 1. A) Bounce trajectory for a water droplet on a pea leaf (diameter 375 µm at velocity 0.93 m s^{-1}). Numbers refer to consecutive bounces after initial impact. B) Re and We criteria for capture or bounce of water and surfactant solutions on pea leaves.

threshold below which velocity all droplets were captured following impact and a bounce threshold above which all droplets bounced following impact.

As would be expected for both water and surfactant solutions, droplets of all sizes and speeds tested were captured by the wettable field bean leaves on first impact. Impact onto bean surfaces previously wetted by other droplets only produced splash for the 1 g litre^{-1} OS surfactant, which also spread extensively and rapidly, occasionally exhibiting exhibiting run-off. A selection of the results obtained for larger droplets on water-repellent pea leaves is given in Table 1. The number of bounces refers only to droplets retained, not to those which bounced off target; a zero value indicates capture on first impact. In these cases, a higher test velocity was not available, so that a bounce threshold was recorded as 'not determined'. Where there was one bounce, the first impact velocity became the bounce threshold and the bounce velocity became the capture threshold if other test velocities were not available. Water droplets always bounced on first impact on pea leaves, even for the smallest droplets (120 µm), with between two and six bounces before retention (Table 1). A typical bounce series is shown in Fig 1A (an aggregate of eight consecutive video frames), which shows a 375 µm droplet travelling at 0.93 m s^{-1} at first impact and bouncing four times before being finally retained on the leaf.

In general, the addition of surfactants increased the droplet capture threshold, resulting in fewer bounces before retention (Table 1); this effect was concentration-dependent. The OS surfactant gave fewer bounces and higher velocity thresholds than the AE surfactants at both 0.2 and 1 g litre^{-1}. There appeared to be a correlation between dynamic surface tension values (maximum bubble pressure method at 5 Hz)[1] and increased capture and bounce thresholds. While the impact time (<2 ms) is not long enough to enable surfactant transport to the new liquid–air surfaces formed during impact, the flight-time before first impact (20 to 80 ms) and between bounce impacts (10 to 60 ms) could have

Table 1. Bulk solution properties, droplet data and impact results for excised pea leaves

Surfactant ($g\ litre^{-1}$)	Bulk surface tension ($mN\ m^{-1}$)		Diameter (μm)	First impact velocity ($m\ s^{-1}$)	Number of bounces	Velocity threshold[b] ($m\ s^{-1}$)	
	Static[a]	Dynamic[a]				Capture	Bounce
None	72	72	864	0.83	3 to 6	0.10	0.18
None	72	72	440	0.71	2 to 5	0.14	0.24
None	72	72	120	0.57	2 to 5	0.19	0.25
AE6 (0.2)	28	69.5	759	1.20	2 to 4	0.22	0.27
AE6 (0.2)	28	69.5	414	0.74	2 or 3	0.27	0.31
AE6 (1.0)	28	68.5	471	0.90	1	0.31[c]	0.90[c]
AE6 (1.0)	28	68.5	419	0.83	0	0.83[c]	nd
AE11 (0.2)	30	67	666	1.67	2 to 3	0.26	0.37
AE11 (0.2)	30	67	445	0.98	0 or 1	0.40	0.98
AE11 (1.0)	30	54	557	1.33	1	0.39[c]	1.33[c]
AE11 (1.0)	30	54	436	0.84	0	0.84[c]	nd
AE20 (0.2)	35	63	836	2.31	2 or 3	0.17	0.25
AE20 (0.2)	35	63	456	1.03	1 or 2	0.25	0.40
AE20 (1.0)	35	55	685	1.47	1	0.38[c]	1.47[c]
AE20 (1.0)	35	55	447	0.80	0	0.80	nd
OS (0.2)	22	63	677	1.24	1 or 2	0.44	0.48
OS (0.2)	22	63	434	0.82	0	0.82[c]	nd
OS (1.0)	22	47	700	1.57	0	1.57[c]	nd

[a] Values from Reference 1.
[b] nd: Not recorded at higher impact velocities.
[c] Results from only a small data set.

allowed some surface tension reduction before impact. Additionally, the elastic or viscoelastic behaviour of the liquid due to the presence of surfactant may have increased viscous damping during impact, which might also have increased the capture threshold. The only splash event recorded for impact onto a previously wetted surface was for 700-μm droplets containing the OS surfactant at 1 g $litre^{-1}$. Droplets of all other solutions were captured when they hit another droplet or a liquid film on the leaf surface.

Droplet and liquid parameters most strongly influencing droplet impact are the droplet diameter (d) and velocity (v), liquid density (ρ), viscosity (μ) and surface tension (γ).[1] These physical properties are described by the dimensionless Reynolds (Re) and Weber (We) numbers: Re $dv\rho/\mu$ and We $= dv^2\rho/\gamma$.

Therefore, one would expect different functions of Re and We to represent the transition points between droplet bounce and capture, as well as between droplet and splash. Such relationships have been found previously; for example, for multiple droplet impact (diameter range 60 to 150 μm, velocity range 12 to 18 m s^{-1}) on a metal wall,[5] the transition from capture to splashing was of the form $We^{0.5}Re^{0.25} > C$, where C is a constant. We as a function of Re for the observed velocity thresholds is shown as a logarithmic plot in Fig 1B. Re and We for these thresholds are strongly grouped and give the following droplet impact criteria for pea leaves: $Re^{1.67}/We = 10^{4.04}$ for capture and $Re^{1.67}/We = 10^{3.3}$ for bounce.

It is often quoted that water droplets with diameters below 100 μm are always 'retained'.[6] However, this is an oversimplification of the physical processes involved. At terminal velocity (0.279 m s^{-1}) their Re (27.9) and We (0.108) place 100 μm droplets in the bounce half of the transition region (Fig 1B); this prediction is supported by the observed behavior of 120-μm water droplets (Table 1). Nevertheless, although such droplets would not be captured on first impact, their bounce distance would be so small that they would almost always be retained on the leaf surface.

The behaviour of a wider range of adjuvants at higher droplet speeds will be used to test these initial hypotheses and results compared directly with polydisperse spray retention behaviour.

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Analysis of surfactant leaf damage using microscopy and its relation to glyphosate or deuterium oxide uptake in velvetleaf (*Abutilon theophrasti*)

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Abstract: Commercial formulations of glyphosate were compared for surfactant leaf damage and glyphosate uptake. The formulations (Roundup® Ultra, Roundup®, and Touchdown® were diluted with water to 12.5 g AI litre^{-1} and applied as 1-μl drops to the first leaf adaxial surface. Tissues at application sites were examined by light, fluorescence and scanning electron microscopy. At 24 h after treatment, tissue necrosis was clearly visible with Ultra and Roundup®, but not with Touchdown®. The application sites of Ultra and Roundup®, but not with Touchdown®. The application sites of Ultra and Roundup® demonstrated a well-demarcated zone of injury showing extensive rupturing of cell membranes in both epidermal and mesophyll cells. Studies using blank formulations without glyphosate confirmed that tissue damage was caused by the surfactant formulants. Diluted formulations (12.5 g AI litre^{-1}) spiked with a minimum of [^{14}C-glyphosate were applied similarly. Time-course studies showed the fastest uptake with Ultra, followed by Roundup® and Touchdown®. Mobilization of glyphosate away from the treated leaf was proportional to uptake. The use of a deuterium NMR method demonstrated that pretreatment of leaves with glyphosate formulations facilitated subsequent leaf loading of deuterium oxide. The extent of the latter correlated with leaf loading of glyphosate in formulations. These results indicate that the role of the surfactant is to overcome the leaf cuticle and membrane barriers to facilitate glyphosate entry into the leaf.

Keywords: glyphosate; surfactant; velvetleaf; uptake; transport; deuterium oxide; NMR.

Glyphosate efficacy is directly related to its ability to penetrate the leaf surface. Surfactants are used routinely in herbicide formulations to improve leaf coverage, wetting and uptake. Glyphosate efficacy, in particular, is strongly influenced by surfactants.[1,2] The delivery efficiency of glyphosate was compared in three commercial formulations. Roundup® Ultra is Monsanto Company's newest formulation in the USA, replacing the previous Roundup® formulation; both formulations contain glyphosate isopropylamine salt in a cationic surfactant. Touchdown® (Zeneca's Canadian formulation) contains the glyphosate trimesium salt in an alkylpolyglucoside surfactant. All of these formulations contain equal concentrations of AI with similar prescribed use rates for weed control.

The microscopy studies examined the tissues at the sites of application of Ultra, Roundup, and Touchdown to leaves of velvet-leaf (*Abutilon theophrasti* (L) Medic). The adaxial surface of the first leaf (3.5–4-leaf plant) was treated with 1-μl drops of the formulations diluted to 12.5 g AI litre^{-1}. The leaves were excised at 24 hours after treatment (HAT), washed with water, and examined for tissue injury. Ultra and Roundup produced visible necrosis, which appeared as bright refractive patches on the leaf surface by epi-illumination stereo microscopy. In contrast, the Touchdown application sites displayed a dark footprint, but remained largely injury-free. The injured sites of Ultra and Roundup also displayed fluorescence when viewed with a fluorescein filter set in the absence of an added fluorochrome dye. Analysis by scanning electron microscopy of the tissue area treated with Roundup clearly showed a well-demarcated and irregularly shaped pit on the leaf surface. Tissue cross-sections of Roundup sites revealed collapsed upper and lower epidermal cell layers and a pycnotic mesenchymal layer.

A minimal amount of [^{14}C]glyphosate (<1% of glyphosate dose) was spiked into each formulation (12.5 g AI litre^{-1}) and applied as 1-μl drops to the adaxial surface of the first leaf (3–4-leaf plants). Uptake (Table 1), which was calculated by summing the radioactivity in the treated leaf and in the rest of the plant, was inversely proportional to that recovered from the treated-leaf wash. Total uptake was fastest with Ultra, reaching 35% of applied dose at 6 HAT and plateauing at 41% by 24 HAT. Roundup showed intermediate uptake followed by Touchdown. Although uptake in Touchdown was initially very low (5% at 6 HAT), it continued throughout the test period and had not reached a plateau by 72 HAT. The amount of radioactivity remaining in the

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